

Polymerizable Derivatives of Long-Chain Fatty Acids. IV.* Vinyl Esters†

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INTRODUCTION

No systematic study of the effect of reaction conditions on the polymerization and on the properties of polymers obtained from vinyl esters of long-chain fatty acids has been published, although there have been a few isolated and conflicting reports.⁴⁻⁹ Fikentscher^{4,5} reported that the vinyl esters of oleic, stearic, and coconut oil fatty acids do not polymerize, whereas Reppe⁶⁻⁸ stated that the vinyl esters of long-chain acids can be polymerized by the usual methods. Beyond brief, qualitative characterization of those polymeric vinyl esters, the literature contains no information on their physical properties. The relative ease with which vinyl esters of long-chain acids can be prepared from plentiful and inexpensive fatty acids, either by acidolysis of vinyl acetate^{1-3,10,11} or by reaction with acetylene,^{6,7} suggested that a thorough study be made of the polymerization and copolymerization of these esters with some commercially important monomers.

In this paper we are reporting: (a) various techniques by which vinyl esters of some long-chain *n*-aliphatic (caprylic, capric, lauric, myristic, palmitic, and stearic) acids can be polymerized by free-radical initiation, (b) methods of isolating and purifying the polymers, (c) qualitative characterization of the polymers, and (d) quantitative description of some of the properties of the polymers, in particular, molecular weights and transition point data. In subsequent reports, the preparation and properties of copolymers will be described.

PREPARATION OF MONOMERS

Vinyl caprylate, caprate, laurate, and myristate were prepared, as pre-

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viously reported,² by acidolysis of vinyl acetate with the appropriate acid. The preparation² of vinyl palmitate and stearate was modified to avoid prolonged heating of the monomers at high temperatures with attendant loss of product as thermal polymer. In the case of these two esters, after removal of excess vinyl acetate and acetic acid and/or anhydride, the residual crude vinyl ester was flash distilled in a modified alembic still similar to that described by Barnitz.¹² The distillate, which contained some free fatty acid, was then dissolved in acetone (3 ml./g. monomer), and 6 *N* aqueous sodium hydroxide in a 5% excess over that required to neutralize free fatty acid was added with vigorous agitation. Insoluble soap was separated by filtration and washed with sufficient acetone to bring the filtrate volume to 4 ml. of solvent per gram of solute. The solution was then cooled to $-20^{\circ}\text{C}.$ for vinyl palmitate and $0^{\circ}\text{C}.$ for vinyl stearate. The monomers were filtered, washed, and dried in an oxygen-free atmosphere.

It is important to note that vinyl esters of unsaturated acids either stop the polymerization or decrease the rate.¹³⁻¹⁵ Table I shows the effect of increasing amounts of vinyl oleate at $75^{\circ}\text{C}.$ in reducing the conversion. Up to about 5% vinyl oleate, no significant decrease occurred. This retarding effect may have been caused by the formation of allyl-types of free radicals¹⁶ from the long-chain, unsaturated portions of the molecule. At $100^{\circ}\text{C}.$, however, gel formation may occur.¹

TABLE I
SOLUTION POLYMERIZATION OF VINYL PALMITATE CONTAINING VINYL OLEATE^a

Vinyl oleate, mole per cent	Conversion to polymer, ^b
0.....	69
1.....	73
5.....	61
10.....	39
25.....	20

^a Polymerization conditions: 2.5 moles benzene per mole monomer(s); 0.5 mole per cent benzoyl peroxide (based on monomer) as initiator; $75^{\circ}\text{C}.$; 7 to 8 hours reaction time; oxygen-free atmosphere.

^b This was calculated from the degree of unsaturation of the solution before and after polymerization, the assumption being made that the double bond of the oleic portion of the molecule did not participate in the polymerization. The conversions as determined by actual isolation of the polymers were from 4 to 7% lower than those calculated.

When divinyl esters of dibasic acids are present in the monomers, even though their content is low, cross-linked, insoluble polymers form. Commercial pelargonic acid (85-90% grade) was the only *n*-aliphatic acid studied which contained significant (although small) quantities of dibasic acids. These could not be separated by fractional distillation alone, and the commercial acid would probably require several hot water washes first, although we have not studied this technique.

In the distillation of the fatty acids, in the preparation of monomers, and during the polymerization reactions, oxygen was excluded. A special grade of cylinder nitrogen (99.9+%) was satisfactory for this purpose.

POLYMERIZATION TECHNIQUES

Four techniques were employed: bulk, dispersion (pearl or bead), solvent, and emulsion polymerization.

Figure 1

BULK POLYMERIZATION OF VINYL LAURATE
AT 65°, 75°, 85° C. 0.25% BENZOYL PEROXIDE

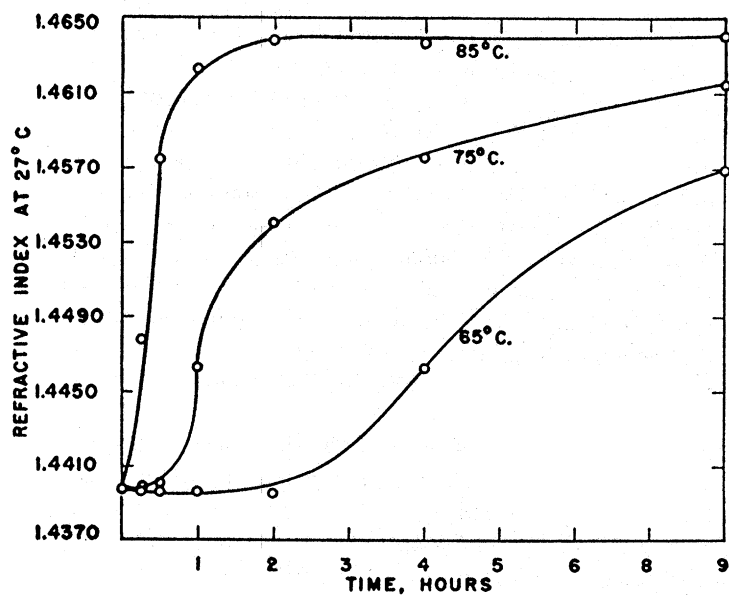
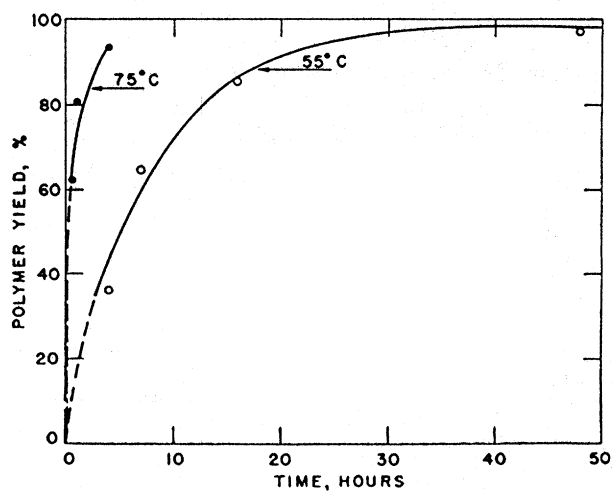


Figure 2

DISPERSION POLYMERIZATION OF VINYL CAPRATE



Bulk polymerizations were conducted at 65°, 75°, and 85°C. with 0.25–0.50 mole per cent of benzoyl peroxide as initiator. Figure 1 shows the course of a typical bulk polymerization of vinyl laurate. As expected, the induction period decreased and the rate of polymerization increased as the temperature was raised. At 85°C., conversion was more than 90% in two hours. These polymerizations were carried out in test tubes immersed in constant-temperature baths at the temperature indicated. The amount of monomer used was usually less than 10 g.; larger scale bulk polymerizations could not be carried out satisfactorily because of poor heat control.

Dispersion or bead polymerizations were conducted by the method of Hohenstein and Mark.¹⁷ 5 parts of an aqueous 1% polyvinyl alcohol solution were used per part of vinyl ester and 0.25 mole per cent of benzoyl peroxide as initiator at 55° and 75°C. Most of the beads obtained were 1 mm or less in diameter. Figure 2 shows the results of the dispersion polymerization of vinyl caprate at 55° and 75°C. Each point on the curve represents an individual polymerization, in which the same stock solution of polyvinyl alcohol and batch of monomer were used, rather than the analysis of a sample withdrawn at intervals. This procedure was necessary for practical considerations because of the amount of polymer required for analysis, molecular weight determination, and other uses. Conversion of vinyl caprate to polymer was more than 90% in three hours at 75°C. and 18 hours at 55°.

Solvent polymerizations were conducted at 75°C. in benzene, ethylbenzene, or carbon tetrachloride, or in mixtures of benzene and ethylbenzene or dodecyl mercaptan. Benzoyl peroxide (0.25 to 1 mole per cent) was used as initiator. Table II shows the results obtained in the polymerization of vinyl laurate in the presence of various quantities of carbon tetrachloride. By varying the quantity of monomer to solvent, in this case an efficient chain-transfer agent, average degrees of polymerization of an extremely low order were obtained. Agreement between cryoscopic molecular weights

TABLE II
CHARACTERISTICS OF LOW MOLECULAR WEIGHT POLYVINYL LAURATES^a

Molar ratio of monomer to CCl ₄	Polymer			Average degree of polymerization
	Cl, %	Molecular weight		
		From end-group ^b	Cryoscopic	
10:1	3.82	3720	—	16-17
2:1	5.45	2600	1966 ^c	9-11
1:1	19.3	736	—	2-3
1:5	27.8	512	—	1-2
1:10	30.4	467	443 ^d	1-2

^a Vinyl laurate polymerized at 75°C. in carbon tetrachloride solution. 1 mole per cent of benzoyl peroxide as initiator; polymerization time 3 hours.

^b Calculated on the assumption that one mole of chain-transfer agent is present per polymer molecule.

^c Cyclohexane as solvent.

^d Benzene as solvent.

and molecular weights calculated from the chlorine analyses (assuming one mole of chain-transfer agent per polymer molecule) was good. The data on chain-transfer reported in this paper are given merely to show the marked effect of a chain-transfer agent on the molecular weight. The vinyl laurate-carbon tetrachloride products are unstable and evolved acidic gases, especially when exposed to light.

The development of a suitable recipe for *emulsion polymerization* of the long-chain vinyl esters presented some difficulties, the major one being the difficulty of achieving stable emulsification both before and throughout the polymerization. The usual emulsifiers, such as soaps and alkylaryl sulfonates, were unsatisfactory. After investigation of a large number of commercially available emulsifiers, it was found that a mixture of non-ionic emulsifiers, such as fatty acid esters of anhydrosorbitol or anhydromannitol, and ionic emulsifiers, such as branched-chain alcohol sulfates, gave the best emulsions. The procedure employed in the preparation of stable emulsions consisted in (a) weighing the monomer and emulsifiers into a flask through which oxygen-free nitrogen was being passed, (b) gently warming and swirling the flask until a uniform mixture had been obtained, (c) transferring the contents of the flask to a high-speed mechanical blender with oxygen-free distilled water, and (d) agitating the mixture at high speed for ten minutes while a stream of oxygen-free nitrogen was being passed continuously into the blender. Emulsion polymerizations were conducted in the usual way in a three-neck flask equipped with an efficient stirrer, a thermometer, and an adapter fitted with a condenser and a gas-inlet tube for nitrogen, while the apparatus was immersed in a constant-temperature bath. Table III shows the standard recipe finally developed. Conversions were 80–99% in seven hours at 55–75°C. The ratio of total emulsifiers to monomer is not critical; as much as 16% and as little as 1% has been used. The emulsifiers shown in Table III do not produce an emulsion with vinyl acetate, whereas with vinyl palmitate approximately 99% of the dispersed phase has a particle size of 1–2 microns.

TABLE III
RECIPE FOR EMULSION POLYMERIZATION OF LONG-CHAIN VINYL ESTERS*

Monomer.....	0.20 mole
Water.....	113 g.
Span 20 ^b	2.8 g.
Tergitol Paste 4 (50%) ^b	5.7 g.
K ₂ S ₂ O ₈	0.001 mole (0.27 g.)

* Reaction time approximately 7 hours at 55–75°C.; conversion >80%.

^b The use of these emulsifying agents does not constitute a recommendation by the U. S. Department of Agriculture of these products over similar products not mentioned.

ISOLATION AND ANALYSIS OF CRUDE POLYMERS

Polymers prepared by the bulk technique were analyzed directly for monomer content by the Wijs iodine number method.²

Polymers prepared by the emulsion technique were isolated by pouring the emulsion into warm saturated sodium chloride solution. The precipitate was dissolved in benzene, and the solution was washed several times with water, dried over anhydrous calcium sulfate, and filtered. A small sample of the solution was evaporated to dryness under vacuum below 55°C. and the residue was then analyzed for unsaturation.²

Polymers prepared by the dispersion technique were dissolved in benzene and then treated as described in the preceding paragraph. In some cases, residual unsaturation was determined on an aliquot portion of the benzene solution which had been diluted to known volume.

Polymers prepared by the solution technique were diluted to a known volume with benzene, and aliquot portions of the solution were then analyzed. When carbon tetrachloride was the solvent, it was removed by vacuum distillation below 55°C., and the residue was analyzed directly for unsaturation and chlorine content.

PURIFICATION OF POLYMERS

A multiple precipitation technique was used. Polymer was dissolved in benzene (5 ml. solvent per gram solute), and the solution was slowly poured into a large volume of precipitant at -5°C. while it was being rapidly swirled by hand. In every case, the volume of precipitant was five times that of benzene. Acetone was the precipitant for the polyvinyl esters of lauric, myristic, palmitic, and stearic (C_{12} to C_{18}) acids and methanol for the polyvinyl esters of caprylic and capric (C_8 and C_{10}) acids. Mechanical or hand stirring was undesirable for the polyvinyl esters of the C_8 to C_{14} acids because precipitated polymer plus much occluded solvent formed on the stirrer in a large clump, thus occluding solubles and preventing efficient contact of the solution with precipitating solvent. The solvent was separated from the viscous, liquid polymers by decantation. Polyvinyl palmitate and stearate, however, precipitated as discrete particles which were filtered, washed with acetone, and dried in air and then under vacuum. Three precipitations were employed in the purification of the polymers reported in Table IV.

That three precipitations were required for complete removal of unconverted monomer was determined by an empirical method. First, from the iodine number of the crude polymer and its weight the quantity of monomer in the crude polymer was calculated. It was assumed that all unsaturation was due to monomer. (This assumption is not strictly correct, but, as will be seen from Table V, it does not vitiate the final result.) Then, after each precipitation the solution was evaporated to dryness, and the residue was weighed. The quantity of monomer in this residue was calculated from its weight and iodine number. In this way a material balance on unconverted monomer was obtained. Table V shows the results of a purification of polyvinyl palmitate. Similar results were also obtained with polyvinyl laurate and caprylate. Since very little, if any,

TABLE IV
MOLECULAR WEIGHTS OF POLYVINYL ESTERS^a

Expt. No.	Ester	Polymerization technique	Conversion, %	Molecular weight Osmometric	Light-scattering
1	Caprylate	Bulk, 75°C., 6 hrs., 0.5 mole % benzoyl peroxide	79	—	143,000
2	"	Solution, 75°C., recipe of Table I footnote <i>a</i>	59	57,000	73,000
3	"	Solution, 75°C., 7 hrs., 0.5 mole % benzoyl peroxide, 1.25 moles benzene, 1.1×10^{-4} mole dodecyl mercaptan	52	—	71,000
4	"	Solution, as No. 3, but 1.0×10^{-3} mole dodecyl mercaptan	31	42,500	54,000
	"	Emulsion, recipe of Table III, 55°C.	96	—	685,000
	"	Emulsion, recipe of Table III, 75°C.	99+	—	870,000
7	Caprate	Dispersion, 75°C., 0.5 hr., 0.25 mole % benzoyl peroxide, polyvinylalcohol solution as dispersant	62	95,000	149,000
8	"	Dispersion, as No. 7 but 1 hr.	81	89,000	263,000
9	"	Dispersion, as No. 7 but 4 hrs.	94	—	741,000
10	"	Dispersion, 55°C., 4 hrs., 0.25 mole % benzoyl peroxide, polyvinylalcohol solution as dispersant	37	61,000	122,000
11	"	Dispersion, as No. 10 but 7 hrs.	65	98,000	215,000
12	"	Dispersion, as No. 10 but 16 hrs.	86	118,000	426,000
13	"	Dispersion, as No. 10 but 48 hrs.	97	165,000	909,000
14	Laurate	Bulk, 75°C., 16 hrs., 0.23 mole % benzoyl peroxide	93	—	314,000
15	"	Bulk, 75°C., 7 hrs., 0.5 mole % benzoyl peroxide	97	—	1,920,000
16	"	Emulsion, recipe of Table III, 55°C.	93	—	685,000
17	"	Emulsion, recipe of Table III, 75°C.	88	—	292,000
18	Palmitate	Bulk, 75°C., 4 hrs., 0.6 mole % benzoyl peroxide	90	—	194,000
19	"	Solution, 75°C., 6.5 hrs., 0.5 mole % benzoyl peroxide, 2.5 moles benzene	82	130,000	119,000
20	"	Solution, as No. 19 but 10 hrs. and 5 moles benzene	64	79,000	79,000
21	"	Solution, as No. 19 but 2.5 moles benzene and 1 mole ethylbenzene	23	—	31,500
22	"	Solution, 75°C., 48 hrs. 1 mole % benzoyl peroxide, 0.1 mole ethylbenzene	99+	—	282,000
23	"	Solution, as No. 22 but 1 mole ethylbenzene	95	—	29,000
24	"	Emulsion, recipe of Table III, 55°C.	80	—	271,000
25	"	Emulsion, recipe of Table III, 75°C.	89	—	278,000

^a Polymers purified by three precipitations from benzene

monomer remained after the third precipitation, three precipitations were employed in all our work.

TABLE V
PURIFICATION OF POLYVINYL PALMITATE^a BY PRECIPITATION WITH ACETONE FROM BENZENE SOLUTION

Number of precipitation	Soluble fraction ^b		Monomer removed ^c	
	Weight, g.	iodine number	Weight, g.	% of that present originally
1	5.6	62.6	3.9	71
2	1.5	63.8	1.1	20
3	0.61	31.8	0.21	4.8
4	0.09	25.3	0.002	0.004
5	0.08	15.3	0.001	0.002

^a 56 g. polyvinyl palmitate, iodine number 8.81 was employed in this experiment. This iodine number corresponds to 9.8% of monomer or 5.5 g.

^b Calculated iodine number of vinyl palmitate, 89.8.

^c Total weight of monomer accounted for in five precipitations was 5.21 g., or 96% of that present originally.

Solvent was removed from purified polyvinyl palmitate and stearate by air and vacuum drying. Purified polyvinyl myristate and laurate were dried by the frozen-benzene technique.¹⁸ This technique was unsuitable for polyvinyl caprylate and caprate because of their low solidification points. Even at $-40^{\circ}\text{C}.$, a mixture of polyvinyl caprylate and benzene eventually melted as the benzene was progressively removed. Polyvinyl caprylate and caprate were freed of solvent by spreading each in a thin film on the inner surface of a flask which was being heated at $50-55^{\circ}\text{C}.$ under high vacuum. After such treatment, the polymers were free of benzene as determined spectrophotometrically.

PHYSICAL MEASUREMENTS

Turbidity measurements necessary for the determination of light-scattering molecular weights were obtained with the photometer developed by Brice.¹⁹ The change of refractive index with concentration, dn/dc , was determined with a differential refractometer.²⁰

In the molecular weight determinations by light-scattering, the solutions were filtered through an ultrafine sintered-glass filter for clarification; neohexane was used as the solvent. The light-scattering molecular weights reported in Table IV were obtained by extrapolating to zero concentration the plot of $H(c/\tau)$ against c (green light of wave length $546\text{ m}\mu$ was used).

Osmotic pressure measurements were carried out in the modified Fuoss-Mead osmometer; benzene was used as the solvent. In nearly all the experiments listed in Table IV, No. 300 gelled cellophane obtained from Sylvania Corporation (the use of this product does not constitute a recommendation by the United States Department of Agriculture) was used. The osmotic pressure molecular weights in Table IV were obtained by extrapolating to zero concentration the plot of π/c against c .

CHARACTERISTICS OF POLYMERS

Molecular Weights

Detailed study of the molecular weights of fractionated and unfractionated polymers will be reported in a subsequent paper. In Table IV, some typical molecular weights are given for polymers prepared by the various techniques. The data in this table were obtained on polymers precipitated three times, as described earlier under "Purification of Polymers."

It is readily apparent that the molecular weights of these polymers are strongly dependent upon the methods of preparation. For example, the polymers prepared by the solution polymerization technique (Table IV, polyvinyl caprylates, experiments 2, 3, 4; polyvinyl palmitates, experiments 19, 20, 21, 22, 23) have substantially lower molecular weights than those prepared by the other techniques. In experiment 22 a polyvinyl palmitate was obtained having a light-scattering molecular weight of only 282,000, even though the conversion was almost 100%. In general, however, the light-scattering molecular weights for the solution-polymerized samples are below 100,000. This may indicate that the growing chains react with the solvent as observed by Mayo and his collaborators²¹ in their study of the solution polymerization of styrene. It is well known that this chain transfer process limits the molecular weight of the polymer and this molecular weight dependence is most noticeable in polymer systems where the active centers of the growing chain are of the reactive type. Since the free radicals on these polymer chains are not stabilized by resonance, it is anticipated that the radicals on these growing chains would be extremely reactive. Thus, if this chain transfer reaction predominates, the molecular weight distribution for polymers prepared by the solution polymerization method should be narrow. This was experimentally verified by the results presented in Table IV for experiments 4, 19, and 20, in which both light-scattering and osmotic pressure methods were employed.

The molecular weights of polymers prepared by the emulsion polymerization technique are also shown in Table IV (polyvinyl caprylates, experiments 5 and 6; polyvinyl laurates, experiments 16 and 17; polyvinyl palmitates, experiments 24 and 25). The weight-average molecular weights are, in general, significantly higher for the polymers prepared by this technique than by the solution method. Since chain transfer processes are important in the polymerization of these monomers, chain transfer to polymer should occur, particularly at the high conversions noted in the table. This being the first description of these vinyl polymers, the main objective was to evaluate polymers prepared at conversions frequently employed in commercial polymer production. At these relatively high conversions, it is probable that these molecular chains are branched because of chain transfer to polymer. These observations substantiate the results obtained on the polymers prepared by the solution method discussed above.

Table IV includes limited information on polymers prepared by bulk polymerization. Since the heats of polymerization for these compounds are apparently high, it is impossible to maintain proper temperature control. The results for the samples prepared by the bulk polymerization technique, however, substantiate the results obtained for the polymers prepared by the other methods. For example, in the preparation of polyvinyl laurate of experiment 15, the conversion reached 97% and an observed weight-average molecular weight of 1,920,000 was obtained; in experiment 14 the conversion was 93% and a weight-average molecular weight of only 314,000 was observed. Because of poor temperature control during bulk polymerization, polymers were also prepared by the dispersion method (experiments 7 through 13). It is clearly evident that as the conversions increase from 37% (experiment 10) to 97% (experiment 13) the weight-average molecular weights increase. This is in complete agreement with the results obtained for polymers prepared by solution, emulsion, and bulk polymerization methods.

It is of interest to note the different dependence of light-scattering molecular weight and osmotic pressure molecular weight on conversion. Since the osmotic method yields a number-average molecular weight and the light-scattering method yields a weight-average molecular weight, these two measurements complement each other by indicating the distribution in molecular size. As the conversion is increased, a greater spread in the two values results. A particularly good example of this phenomenon is shown by the polyvinyl caprate polymers (experiments 7 through 13, Table IV). At a conversion of 62% the number-average molecular weight was 95,000, whereas the weight-average molecular weight was 149,000. When the conversion was 97%, however, the number-average molecular weight was 165,000, and the weight average was almost 1,000,000. These observations are in agreement with the conclusions reached concerning the significance of the chain transfer process between a growing chain and polymer.

Because of the high reactivity of the free radical, many chain transfer processes occur during the early phases of the polymerization. These may be chain transfer to monomer, chain transfer to impurities such as inhibitors, chain transfer to the solvent or water. Thus, these reactions may control the molecular size of the polymer by terminating the growing chain. As the polymerization process continues, however, a high concentration of polymer is formed. These polymer molecules can be reactivated, extending the polymerization process. At the extremely high conversions, it is apparent that some molecules are reactivated many times before the polymerization process is terminated. The probability of a chain transfer reaction to polymer, therefore, may increase as the size of the polymer molecule increases.

Also of interest is the influence of benzene, ethylbenzene, carbon tetrachloride, and dodecyl mercaptan on molecular weight and degree of conversion (experiments 2-4, 19-23, Table IV). By selection of polymeriza-

tion techniques and reaction conditions, a wide range of products can be readily obtained.

Solubility

Polyvinyl esters of the C_8 through C_{18} saturated aliphatic acids are soluble in aliphatic and aromatic hydrocarbons (such as neohexane, petroleum ethers, benzene, and toluene) and, with the exception of polyvinyl caprylate, are insoluble in acetone and short-chain alcohols. Polyvinyl caprylate is slightly soluble in acetone.

Intrinsic Viscosities

The intrinsic viscosities of the higher polyvinyl esters are low. Table VI lists the intrinsic viscosities in neohexane for some polyvinyl esters of different weight-average molecular weights.

TABLE VI
INTRINSIC VISCOSITIES OF POLYVINYL ESTERS IN NEOHEXANE

Expt. No. from Table IV		Molecular weight	Intrinsic viscosity
18	Polyvinyl palmitate	194,000	19.2
25	" "	278,000	24.5
24	" "	271,000	26.9
14	Polyvinyl laurate	314,000	27.4
17	" "	292,000	29.8
16	" "	685,000	42.8
1	Polyvinyl caprylate	143,000	20.2
5	" "	685,000	41.8

Transition Points

The polyvinyl esters of the C_8 through C_{18} acids may be described qualitatively as viscous liquids (polyvinyl caprylate, caprate, and laurate) or wax-like solids (polyvinyl myristate, palmitate, and stearate) at 25°C. The first-order transition points were determined on purified polymers both refractometrically²² (Fig. 3 and Table VII) and by the appearance or disappearance of double refraction while cooling or heating the specimens on the stage of a polarizing microscope (Table VII). Excellent checks were obtained. By both techniques, a hysteresis effect was noted. Thus, as the temperature of the specimens was increased, the appearance of a line of demarcation in the refractometer and the disappearance of double refraction occurred at a higher temperature than did the break in the curves of Figure 3 or the reappearance of double refraction.

The similarity between the refractive index-temperature curves of the polyvinyl esters and polycetyl acrylate²² is pronounced. In the polyvinyl esters, however, we believe that a first-order transition point and not a second-order transition point is being measured because of the close corre-

spondence between the data obtained refractometrically and with the polarizing microscope. It is likely that crystallization of the alkyl side-

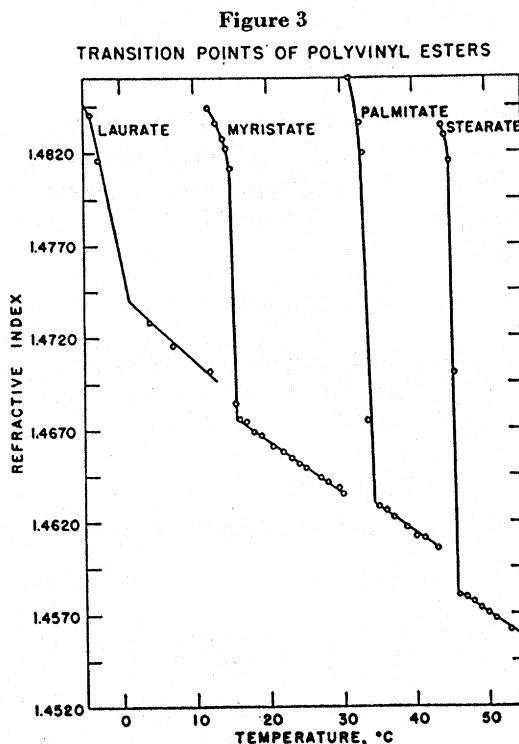


TABLE VII
FIRST-ORDER TRANSITION POINTS OF SOME POLYVINYL ESTERS

Polyvinyl ester	Transition point, °C.			
	Refractometric method		Polarizing microscope method	
	A ^a	B ^b	A ^c	B ^d
Caprylate (Expt. 2, Table IV)	None observed above -30°		—	—
Caprate (Expt. 12, Table IV)	None observed above -30°		—	—
Laurate (bulk, 100°C.)	—	1	—	—
Myristate (bulk, 75°C.)	28.5	15.5	—	—
Palmitate (Expt. 19, Table IV)	40.5	34.5	40.5-41.2	34-38
Stearate (bulk, 75°C.)	51.7	45.6	50.5-51.2	44.0-46.5

^a Temperature of appearance of first line of demarcation in the field of the refractometer (temperature increasing).

^b Temperature taken from break in curves of Figure 3 (temperature decreasing).

^c Temperature of disappearance of double refraction (temperature increasing).

^d Temperature of reappearance of double refraction (temperature decreasing).

chains occurs in the polyvinyl esters. A similar interpretation has been reported by Kaufman, Sacher, Alfrey, and Fankuchen²³ for higher acrylates.

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Synopsis

Contrary to some published reports, the vinyl esters of saturated fatty acids polymerize readily and rapidly. Vinyl oleate, when present in excess of 5%, and oxygen exert marked retarding effects.

Techniques are described for the free-radical-initiated polymerization of the vinyl esters of caprylic, capric, lauric, myristic, palmitic, and stearic acids in bulk, dispersion, solution, and emulsion. Some data are given for polymerization in the presence of chain-transfer agents, such as carbon tetrachloride, dodecylmercaptan, and ethylbenzene. Conditions are reported for obtaining degrees of polymerization from about 2 (when chain-transfer agents are employed) to 10,000 (weight average). The weight average degree of polymerization increases markedly as the conversion increases, particularly above 80%. Even up to extremely high conversions, soluble polymers are obtained in most cases.

Solubility characteristics, transition point data, molecular weights (osmometric and light-scattering), and isolation and purification techniques are also reported.

Résumé

Contrairement à certaines publications, les esters vinyliques des acides gras saturés polymérisent rapidement et facilement. L'oléate de vinyle à une concentration supérieure à 5%, de même que l'oxygène exercent une action retardatrice marquée. Les techniques de polymérisation initiée par des radicaux libres sont décrites pour les esters

caprylique, caprique, laurique, myristique, palmitique et stéarique, tant en bloc, en suspension, en solution qu'en émulsion. Des résultats sont donnés pour les polymérisations, exécutées en présence d'agents de transfert de chaîne, tels que le tétrachlorure de carbone, le mercaptan dodécylique et l'éthylbenzène. Les conditions sont indiquées pour obtenir des degrés de polymérisation variables, de deux (si on utilise des agents de transfert de chaîne) à 10,000 (moyenne en poids). Le poids moléculaire moyen en poids croît nettement avec le taux de conversion de la réaction, surtout au delà de 80% de rendement. Même aux rendements les plus élevés, les polymères obtenus sont solubles dans la plupart des cas. Les caractéristiques de solubilité, des points de transition, de poids moléculaires (osmotiques, et par diffusion de la lumière) sont renseignées; de même l'isolement des produits et leur purification sont décrits.

Zusammenfassung

Im Gegensatz zu einigen in der Literatur erschienenen Mitteilungen polymerisieren Vinylester gesättigter Fettsäuren bereitwillig und schnell. Mehr als 5% Vinyloleat, oder Sauerstoff üben einen merkbar verspätenden Einfluss aus. Es werden Methoden für die durch Freiradikale initiierte Polymerisation der Vinylester von Capryl-, Caprin-, Laurin-, Myristin-, Palmitin-, und Stearinsäure in Blockpolymerisation, in Dispersion, in Lösung und in Emulsion beschrieben. Es werden einige Daten der Polymerisation in Gegenwart von Kettenübertragungsmitteln wie Tetrachlorkohlenstoff, Dodecylmercaptan und Äthylbenzol gegeben. Bedingungen zur Erzielung von Polymerisationsgraden in Bereich von ungefähr 2 (wenn Kettenübertragungsmittel benutzt werden) bis 10,000 (Gewichtsmittel) werden berichtet. Der Gewichts-Mittel-Polymerisationsgrad nimmt mit ansteigendem Umsatz, besonders oberhalb 80%, stark zu. Sogar bis zu einem extrem hohen Umsatz werden in den meisten Fällen lösliche Polymere erhalten. Löslichkeitseigenschaften, Umwandlungspunkt-Daten, Molekulargewichte (aus osmotischen und Lichtstreuungsmessungen) und Isolations- und Reinigungsmethoden werden ebenfalls angegeben.